[Bu^tNHP(μ-NBu^t)_2PNH_2], a novel building block for neutral and anionic polycyclic main group arrangements†

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The novel precursor [Bu^tNHP(μ-NBu^t)_2PNH_2] (**1**) provides easy access to polycyclic main group systems; reaction with Sb(NMe_2)_3 gives the tricyclic species {[Bu^tNHP(μ-NBu^t)_2-P]_2{Me_2NSb(μ-N)}_2] (**2**), whereas reaction with an excess of Bu^nLi results in elimination of LiNH_2 and the formation of the co-complex [{Bu^tNP(μ-NBu^t)_2P}_2N]Li_3·(Bu^nLi)_2, (**3**), containing the unprecedented [{Bu^tNP(μ-NBu^t)_2P}_2N]^{3-} trianion.

In recent years the synthesis and coordination chemistry of a range of new anionic ligands based on p-block element frameworks has become a rich area of study. This work has been dominated by a number of related Group 15 and 16 element/ nitrogen arrangements, such as the tripodal systems [E(NR)_3]^{2-} (E = S–Te)[1] and [E(NR)_3]^{3-} (E = As, Sb),[2] which provide the means to an extensive range of cage complexes, containing well-defined mixed-element compositions.[2] Such cages have potentially far-ranging applications as single-source materials to a number of technologically important mixed-element phases.[3] The normally easy access to these multifunctional p-block element ligand arrangements contrasts with the generally far more involved synthetic procedures required to prepare related systems based on carbon. However, a key issue is whether systematic routes can be devised to more elaborate polyfunctional p-block element species (beyond the simple systems previously investigated). To this end, we present here a simple design approach to a family of polycyclic Group 15 imido frameworks, providing a new direction in this area.

The principal starting material for these investigations, [Bu^tNHP(μ-NBu^t)_2PNH_2] (**1**), is prepared in good yield (59%) by the reaction of [Bu^tNHP(μ-NBu^t)_2PCl][4] with NH_3(g) in THF solution.† Previous studies of imido phosphorus anions have dealt almost exclusively with species of the type [R'NP(μ-NR)]_2^{2-}, prepared by deprotonation of [R'NHP(μ-NR)]_2.[5] Although **1** has a similar P_2N_2 core arrangement to the latter, it presents the unique opportunity for deprotonation at up to three positions (*i.e.* the Bu^tNH and NH_2 groups). The reaction of **1** with Sb(NMe_2)_3 (1:1 equiv.) in toluene gives [{Bu^tNHP(μ-NBu^t)_2P}_2{Me_2NSb(μ-N)}_2] (**2**) (Scheme 1). This result is similar to that observed between simple primary amines (RNH_2) and Sb(NMe_2)_3,[6] which gives dimers of the type [Me_2NSb(μ-NR)]_2. However, in the case of **2** a tricyclic arrangement is established in a single step. The low reactivity of the Bu^tNH protons in **2** (which could potentially react further with the Sb-bonded NMe_2 groups) contrasts with the deprotonation of **1** with Bu^nLi (1:3 equiv., respectively). The product is the unusual co-complex [{Bu^tNP(μ-NBu^t)_2P}_2N]Li_3·(Bu^nLi)_2 (**3**), the framework of which results from a combination of deprotonation and coupling of the dimer units of **1** (with elimination of LiNH_2) (see ESI†).

The low-temperature X-ray structures of **1**, **2** and **3** were obtained.‡ Although simple, **1** is the first non-symmetrically substituted cyclophosphazane containing the NH_2 functionality (Fig. 1). Related species containing the NH_2 functionality are
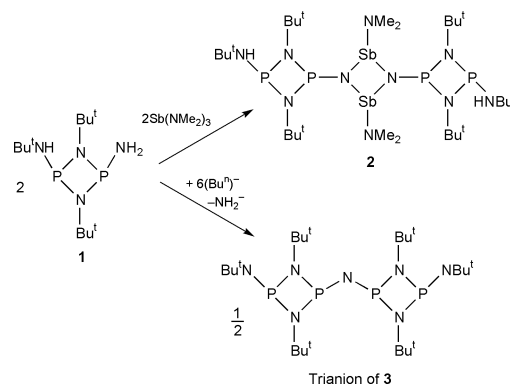
Scheme 1

rare[7] and the only structurally characterised dimers previously reported are chlorides of the type [R_2NP(μ-NR')(μ-NR'')PCl][8] and [Bu^tNHP(μ-NBu^t)_2PCl][4] (the immediate precursor to **1**). The *cisoid* disposition of the Bu^tNH and NH_2 groups found in molecules of **1** is similar to that observed for the previous chlorides. However, the similarity of the ^1H and ^31P NMR behaviour of **1** in toluene solution with that of [PhNHP(μ-NPh)]_2 suggests that two closely related *cisoid* isomers are present (in *ca.* 2:1 ratio, corresponding to rotation of the Bu^tNH group *exo* or *endo* to the P_2N_2 ring).[9]

Complex **2** (Fig. 2) has a tricyclic arrangement composed of a central Sb_2N_2 ring symmetrically substituted with bridging [Bu^tNHP(μ-NBu^t)_2P] groups. The orientation of these ring units approximately *trans* to the Sb_2N_2 ring plane gives molecules an overall S-shape, in which the *cisoid* conformation found in the precursor **1** is retained in the [Bu^tNHP(μ-NBu^t)_2PN] ring units of **2**. The bias for the *cisoid* conformation of these substituents is apparently reinforced by H-bonding of the terminal Bu^tNH protons to the *trans* Me_2N groups of the Sb_2N_2 core [N(2)···N(5) 3.178(9) Å (H(2)···N(5) 2.34 Å), N(2)H(2A)···N(5A) 165.3°]. Although (unlike **1**) the
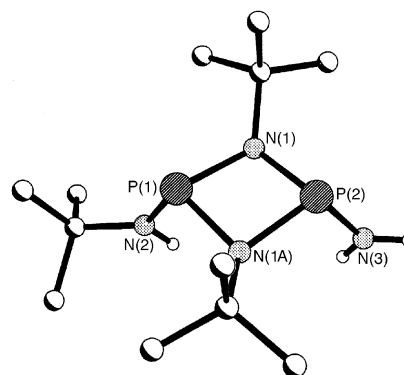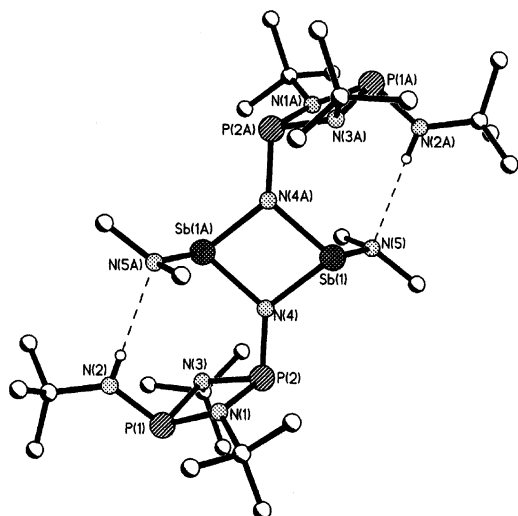

Fig. 1 *Cisoid* conformation of molecules of **1**. Key bond lengths (Å) and angles (°): P(1)–N(1) 1.728(1), P(2)–N(2) 1.663(2), P(2)–N(1) 1.729(1), P(2)–N(3) 1.663(2); N(1)–P(1)–N(2) 105.54(7), N(1)–P(1)–N(1A) 80.79(9), N(1)–P(2)–N(3) 105.81(8), N(1)–P(2)–N(1A) 80.78(9), P(1)–N(1)–P(2) 97.48(7).

Fig. 2 Tricyclic molecules of **2**. Key bond lengths (Å) and angles (°): Sb(1)–N(4) 2.071(9), Sn(1)–N(4A) 2.048(9), Sb(1)–N(5) 2.06(1), P(2)–N(4) 1.680(9), P(2)–N(1) 1.726(9), P(2)–N(3) 1.729(9), P(1)–N(1) 1.739(9), P(1)–N(3) 1.778(9), P(1)–N(2) 1.66(1), N(2)···N(5) 3.178(9) [H(2)···N(5) 2.34, N(2)H(2A)···N(5A) 165.3]; N(4)–Sb(1)–N(4A) 77.3(4), Sb(1)–N(4)–Sb(1A) 102.7(4), N(4,4A)–Sb(1)–N(5) mean 100.2, Sb(1)–N(4)–P(2) 130.5(5), Sb(1A)–N(4)–P(2) 126.8(5), N(4)–P(2)–N(1) 108.3(5), N(4)–P(2)–N(3) 101.0(4), N(1)–P(2)–N(3) 82.5(4), P(2)–N(1,3)–P(1) mean 97.6, N(1)–P(1)–N(3) 80.8(4), N(2)–P(1)–N(1,3) mean 105.0.

[Bu^{t}NHP(μ-NBu^t)$_2$PN] units of **2** are no longer symmetric, deprotonation of the NH$_2$ group of the precursor has comparatively little effect on the overall bond lengths and angles found in these units.

The surprising result of attempted deprotonation of **1** with Bu^{n}Li is the formation of the elaborate cage complex **3**, consisting of a [{Bu^{t}NP(μ-NBu^t)$_2$P}$_2$N]$^{3-}$ trianion coordinated to three Li$^+$ cations and further associated with two monomer units of Bu^{n}Li (Fig. 3). Although uncommon, a number of co-complexes with Bu^{n}Li of this kind have been structurally characterised in recent years.[10] The composition of **3** resembles that of [Al$_2$(NHBu^t)$_3$(NBu^t)$_3$Li$_3$·2Bu^{n}Li], which contains an [Al$_2$(NHBu^t)$_3$(NBu^t)$_3$]$^{3-}$ trianion unit and two Bu^{n}Li monomers.[11c] Nonetheless, the bicyclic [{Bu^{t}NP(μ-NBu^t)P}$_2$N]$^{3-}$ trianion is an unprecedented Group 15 imido ligand arrangement. The closest comparison that can be made with the trianion framework of **3** is with the neutral cyclophosphazane
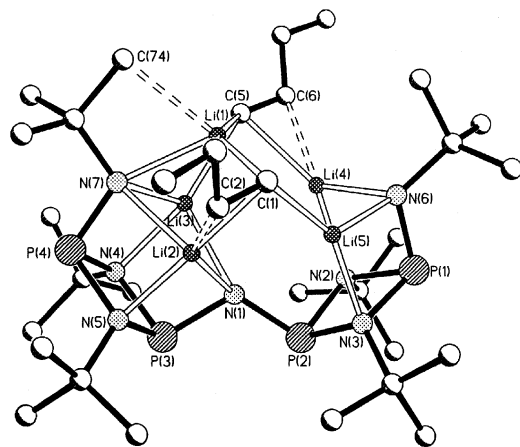
Fig. 3 Cage structure of the co-complex **3**. Key bond lengths (Å) and angles (°): within the [{Bu^{t}NP(μ-NBu^t)P}$_2$N]$^{3-}$ trianion: P(1)–N(6) 1.655(3), P(1)–N(2) 1.792(3), P(1)–N(3) 1.784(3), P(2)–N(2) 1.774(3), P(2)–N(3) 1.762(3), P(2)–N(1) 1.676(3), P(3)–N(1) 1.689(3), P(3)–N(4) 1.768(2), P(3)–N(5) 1.768(2), P(4)–N(4) 1.779(2), P(4)–N(5) 1.785(2), P(4)–N(7) 1.668(3); N(2,4)–P(1,4)–N(3,5) mean 82.3, N(2,4)–P(2,3)–N(3,5) mean 83.3, P(2)–N(1)–P(3) 113.1(1); within Li–N/C framework: terminal Bu^{t}N–Li(2,3,4,5) range 1.987(6)–2.208(6), μ-Bu^{t}N–Li(2,3,4,5) range 2.014(6)–2.102(6), N(1)–Li(2) 2.313(6), N(1)–Li(3) 2.193(7), N(7)–Li(1) 2.147(7), C(1,5)–Li(2,3,4,5) range 2.124(7)–2.218(6), C(1,5)–Li(1) mean 2.26, C(2)···Li(2) 2.461(6), C(6)···Li(4) 2.341(6), C(74)···Li(4) 2.783(6).

[{PhNHP(μ-NPh)$_2$P}$_2$NPh] (a product of condensation of PhNH$_2$ with PCl$_3$), consisting of a similar arrangement of two P$_2$N$_2$ rings linked by an NPh bridge.[11] All five of the Li$^+$ cations of **3** have distinct coordination geometries. The positioning of Li(2) and Li(3), and Li(4) and Li(5) within the 'hemisphere' of the coordinating [{Bu^{t}NP(μ-NBu^t)P}$_2$N]$^{3-}$ trianion of **3** is broadly similar. Each of these cations is coordinated by one of the μ-NBu^t groups and by the terminal Bu^{t}N group of the [Bu^{t}NP(μ-NBu^t)P] halves of the trianion unit. However, presumably owing to the geometric constraints involved, the μ-N centre linking the [Bu^{t}NP(μ-NBu^t)P] units [N(1)] only bonds to Li(2) and Li(3) [cf. > 2.84 Å for Li(4,5)···N(2)], giving a pseudo-cubane fragment on this side of the molecule which is reminiscent of the structure of [{Bu^{t}NP(μ-NBu^t)}$_2$Li$_2$·2THF].[5b] The two Bu^n groups bridge Li$^+$ cations associated with each [Bu^{t}NP(μ-NBu^t)P] half of the trianion. The involvement of the α-C and β-C centres of each of the Bu$^n-$ anions with Li(2) and Li(4) is similar to that found in the hexameric structure of [Bu^{n}Li]$_6$ in the solid state [β-C(–H)···Li ca. 2.28 Å;[12] cf. C(2)···Li(2) 2.461(6) and C(6)···Li(4) 2.341 (6) Å in **3**]. The remaining Li cation [Li(1)] is located above the pseudo-cubane half of the cage, being bonded to the α-C atoms of both of the (Bu^n)$^-$ anions and to a terminal Bu^{t}N group. Further agostic interaction with the Me group of this Bu^{t}N ligand [C(74)···Li(1) 2.783(6) Å[15] results in a pseudo-tetrahedral geometry for Li(1).

Notes and references

‡ CCDC reference number 150926-150928. See http://www.rsc.org/supp-data/cc/b0/b009000j/ for crystallographic data in .cif or other electronic format.

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